PROCESS OF MATERIAL REDOX SYNTHESIS
COAT WITH CARBON A CUTS CONTROLEE
FIELD OF THE INVENTION
The present invention relates to a method of preparation of materials of electrode able to allow reactions < RTI ID=1.1> rédox< /RTI> by exchange of alkaline ions and electrons. Les applications sont dans le domaine des générateurs électrochimiques (batteries) primaires ou secondaires, des générateurs de type supercapacités et dans le domaine des systèmes de modulation de la lumière de type < RTI ID=1.2> électrochrome.< /RTI>

FORMER ART
The compounds of insertion of LiMPO4 formula of structure olivine where M is a metal cation pertaining to the first line of metals of transition for example mn, Fe, Co or Ni, are known and their use as material of cathode in the batteries with lithium was reported by < RTI ID=1.3> Goodenough< /RTI> and Al in patent US-A-5.910.382. In Canadian request CA-A-2.307.119, the general information of composed " of < type; RTI ID=1.4> LiMP04 " a< /RTI> summer specified insofar as while keeping the same structure olivine appreciably, part of the atoms M can be substituted by other metals of valence ranging between 2 and 3, of which the close transition metals or part of phosphorus, can be substituted by elements such as If, S, < RTI ID=1.5> Al, < /RTI> Have. In the same way, lithium allowing < RTI ID=1.6> the électroneutralité< /RTI> can occupy a fraction or the totality of the octahedral sites of the structure olivine, or possibly place themselves in interstitial position when the totality of the octahedral sites is occupied.

The formula < RTI ID=1.7> Lix+yMl- (y+d+t+q+r) DdTtQqRr [Po4] L (p+s+v) [So4] p [SiO4] S [VO4] dans< /RTI> which: < RTI ID=1.8> -

M< /RTI> can be Fe2+ or < RTI ID=1.9> Mn2+< /RTI> or a mixture of both; - D can be a metal in the state of oxidation +2 selected in the group containing < RTI ID=2.1> Mg2+, < /RTI> Ni2+, Co2+, Zn2+, < RTI ID=2.2> Cu2+< /RTI> and Ti2+; - T can is a metal in the state of oxidation +3 selected in the group containing < RTI ID=2.3> A13+< /RTI> < RTI ID=2.4> Ti3+< /RTI> < RTI ID=2.5> Cr3+< /RTI> Fe3+ Mn3+ Ga3+ and V < RTI ID=2.6> ; < /RTI> - Q is a metal in the oxidation step +4 selected in the group containing < RTI ID=2.7> Ti4+, < /RTI> < RTI ID=2.8> Ge4+, < /RTI> < RTI ID=2.9> Sn4+< /RTI> and V4+; et -R est un métal dans l'état d'oxydation +5 choisi dans le groupe contenant < RTI ID=2.10> Vus+,< /RTI> < RTI ID=2.11> Nib5+< /RTI> and < RTI ID=2.12> Ta5+, < /RTI> with a definition of parameters X, y, < RTI ID=2.13> D, < /RTI> < RTI ID=2.14> T, < /RTI> Q, R, p, S and include the general information of the direction to be given to the < RTI ID=2.15> term " de< /RTI> LixMXO4 type, 0 < RTI ID=2.16> vx < 2 " of skucture olivine< /RTI> within the meaning of the present invention and will be used in what follows. The preferred substituents phosphorus are silicon and sulphur.

In these compounds prepared in form < RTI ID=2.17> lithiés< /RTI> < RTI ID=2.18> (à< /RTI> the discharged state), at least one of metals of transition is with the state of oxidation < RTI ID=2.19> II.< /RTI> In patent US-A-5.910.382 and its < RTI ID=2.20> CIP) < /RTI> like in the following patents and publications, the syntheses of made up the < RTI ID=2.21> LiNT04< /RTI> all are carried out starting from a salt of the metal of transition M corresponding to the oxidation step < RTI ID=2.22> II< /RTI> and by preserving this state of oxidation throughout the synthesis to the end product. The transition metal which one maintains valence II whole during the synthesis, whatever the followed way, is the iron of which the majority of made up oxidize spontaneously. < RTI ID=2.23> #< /RTI> <RTI ID=2.24>l'air</RTI> for example, < RTI ID=2.25> LiFeP04< /RTI> was realized by reaction in a solid state, high temperature and under inert atmosphere of the various components (for example for the source of iron, Fe (OOCCH3) 2, the source of phosphate, < RTI ID=2.26> NH4H2P04< /RTI> and that of lithium, < RTI ID=2.27> Li2C03). < /RTI> In all the cases, the source of iron is a salt in which iron with the state of oxidation II, that it starting from iron N acetate like is described in patent US-A-5.910.382, of iron II oxalate like is described in < RTI ID=2.28> Electrochem< /RTI> and Solid-State Letters, 3,66 (2000) and in Proc. lOth < RTI ID=2.29> IMLB, < /RTI> Como, Italy, May (2000) or of vivianite (Fe3 < RTI ID=2.30> (PO4) < /RTI> < RTI ID=2.31> 2< /RTI> < RTI ID=2.32> 8H2O) < /RTI> as described in the Canadian request for patent CA-A-2.270.771.

Sensitivity of iron
II with respect to oxidation by oxygen all these processes of synthesis make very delicate and all the precautions must be taken to completely remove the presence of oxygen and in particular during the heat treatment, which increases the cost of corresponding material. This sensitivity gives place has a < RTI ID=3.1> irreproductibilité< /RTI> electrochemical behavior of the samples. This problem is underlined in
Yamada and Al J. < RTI ID=3.2> Electrochem< /RTI> Ploughshare, 148, A224 (2001). In addition, iron is the most useful element, from its abundance and absence of toxicity, and the principal implementation of the invention is intended for a preparation improved of made up < RTI ID=3.3> rédox </RTI> containing this element. It is obvious that the results of the invention apply to manganese, vanadium, cobalt, titanium, vanadium etc under conditions corresponding to their desired oxidation step. Generally, any precursor of the metal M of which the least expensive the oxidation step is easiest to handle does not correspond to that necessary in the formula of the material < RTI ID=3.4> rédox< /RTI> < RTI ID=3.5> LiXMX04.< /RTI>

An improvement of these compounds was previously proposed in the patent
CA-A-2.270.771). In this document, it was shows that the electrochemical performances of LiFeP04 were largely improved that it is in reversible term of capacity, of < RTI ID=3.6> cyclabilité< /RTI> or of power, when the particles of material are covered with a fine layer with electronic conducting carbon.

In this request, the inventors made profitable makes it use an iron salt to the state of oxidation < RTI ID=3.7> II, < /RTI> en présence d'un composé organique susceptible < RTI ID=3.8> d'être</RTI> pyrolysis, under the conditions of the synthesis, without however that the carbon residue cannot be oxidized because it weak capacity oxidizing of the ferrous compound or the atmosphere in balance with this last.

The patent application EP-A-1.094.532 describes a method for the production of materials for an active positive electrode. This method includes a stage of < mixture; RTI ID=3.9> of une< /RTI> plurality of substances to obtain a precursor. Then the precursor is calcining to lead to the synthesis of a compound of formula LiX < RTI ID=3.10> MyP04< /RTI> in which X is higher than 0 and less than or equal to 2, there is equal to or higher than 0,8 and less than or equal to 1,2 and M includes at least an orbital metal having 3D. A solid reducing agent is added during the stage of mixture to that the precursor in order to allow the preparation, which is carried out under inert atmosphere, of

material for active positive electrodes able to dope and of < RTI ID=4.1> dédoper</RTI> in a satisfactory and reversible way lithium.

EP-A-1.094.533 describes an not-aqueous electrolyte adapted for the secondary batteries using a material or an electrode activates containing a compound represented by the general formula < RTI ID=4.2> LixMyP04, dans</RTI> which X is higher than 0 and less than or equal to 2, and is there equal to or higher than 0,8 and less than or equal to 1,2, with
M containing a state of transition 3D, size of the grains of < RTI ID=4.3> LiXMyP04</RTI> is not higher than 10 micrometers. This nonaqueous electrolyte for secondary batteries is presented like having cyclic characteristics improved and high of capacity.

International request PCT referred WO < RTI ID=4.4> 01/53198</RTI> described a material, containing mixed compound lithium metal, which releases by electrochemical interaction of the ions lithium. This material is prepared starting from the precursors necessary by reduction of at least one of the metal ions by carbon
In addition to their electrochemical performance in the accumulators with lithium, the interest of this new family of materials is to bring into play elements not-poisons, abundant and inexpensive to extract. These characteristics are determining for the development of large accumulators to lithium applicable in particular to the market of the electric vehicle for which the need becomes pressing with accumulation in the environment of gases for purpose of greenhouse.

There is thus a need for the development for a new process simpler and more reproducible, cheaper than those already known while offering improved performances, in particular, for all new technique making it possible to manufacture large quantities of material without losing the quality control, dependent on the purity of the phases obtained and obtaining granulometry adapted in particular to the electrochemical applications, this in a reproducible way.

SUMMARY OF THE INVENTION
The present invention describes a process of synthesis of composed of formula < RTI ID=5.1> LixM, - yM' y</RTI> < RTI ID=5.2> (X04) </RTI> < RTI ID=5.3> N, </RTI> par mise en équilibre dans les proportions requises d'un mélange comprenant des précurseurs des constituants du composé et la réduction du mélange équilibré des précurseurs avec une atmosphère gazeuse réductrice. The initial mixture can be added with a source of carbon what allows the preparation, with made up of < RTI ID=5.4> fonnule</RTI> < RTI ID=5.5> LixMi-yM' y (X04) N sous</RTI> the shape of a material made up of grains coated with carbon. The material thus obtained has

excellent a size and a controllable form of the grains and their conductivity.

These materials are usable for the preparation in particular of electrochemical cells including/understanding an electrolyte and at least two electrodes of which at least one includes/understands at least a material synthesized according to one of the processes of the invention.

SHORT DESCRIPTION OF THE DRAWINGS

Appear < RTI ID=5.6> 1: leur< /RTI> cycle obtained by < RTI ID=5.7> voltamétrie< /RTI> slow < RTI ID=5.8> (v = < /RTI> 20 mV. < RTI ID=5.9> h~l) < /RTI> with < RTI ID=5.10> 80 C< /RTI> for a battery containing noncarbonaceous $LiFePO_4$ synthesized starting from < RTI ID=5.11> $FePO_4$.< /RTI> < RTI ID=5.12> $2H_2O$< /RTI> (reduction by hydrogen) (full features) compared with the same sample after carbonization (milked dotted lines).

Figure 2: Morphology of carbonaceous $LiFePO_4$ synthesized starting from $FePO_4$. < RTI ID=5.13> $2H_2O$< /RTI> (reduction by hydrogen). Micrography taken under the electron microscope with sweeping enlargement X 5.000.

Figure 3 < RTI ID=6.1>: Sow cycle< /RTI> obtained by < RTI ID=6.2> voltamékie< /RTI> lente (v = 20 mV. h-1) at 80 C of a battery containing < RTI ID=6.3> $LiFePO_4$< /RTI> carbonaceous synthesized starting from < RTI ID=6.4> $FePO_4$.< /RTI> < RTI ID=6.5> $2H_2O$< /RTI> (reduction by hydrogen) (full features) compared a < RTI ID=6.6> $LiFePO_4$< /RTI> obtained according to CA-A-2,270,771 followed by a stage of carbon deposit (milked dotted lines).

Figure 4: Profiles of load and discharge carried out in galvanostatic mode with
80 C and two-speed of load and discharge (C/8: full features and Milked C/2 dotted lines) for batteries containing carbonaceous $LiFePO_4$ synthesized starting from $FePO_4$. < RTI ID=6.7> $2H_2O$< /RTI> (reduction by hydrogen).

Figure 5: Evolution of the capacity to the cycling of a battery containing
Carbonaceous $LiFePO_4$ synthesized starting from $FePO_4$. $2H_2O$ according to 1 ' example
2 (reduction by < RTI ID=6.8> hydrogen) - Voltamétrie< /RTI> slow < RTI ID=6.9> (v= 20< /RTI> mV. h-1) with
80 C of a battery containing $LiFePO_4$ synthesized from
$FePO_4$. < RTI ID=6.10> $2H_2O$< /RTI> (reduction by carbon).

Figure 6 : < RTI ID=6.11> Seme< /RTI> cycle obtained by < RTI ID=6.12> voltammétrie< /RTI> slow (v = 20 mV. h-1) with < RTI ID=6.13> 80 C< /RTI> batteries containing carbonaceous LiFePO4 synthesized from
FePO4. < RTI ID=6.14> 2H2O< /RTI> (reduction by CO/CO2). 1/1) for samples containers various percentages of carbon (0.62% : full features,
1.13% features dotted lines, 1.35% fatty features).

Figure 7: Electronic microscopy with sweeping-Nanoparticules < RTI ID=6.15> aglomérées< /RTI> of < RTI ID=6.16> FePO4# 2H2O< /RTI> Budenheim (E53-81 rank).

Figure 8: Microscopie MEB showing a particle of the LiFePO type obtained by reaction in a solid state enters the agglomerated nanoparticules < RTI ID=6.17> FePO4# 2H2O< /RTI> Budenheim (rank < RTI ID=6.18> E53-81) < /RTI> and the < RTI ID=6.19> Li2CO3< /RTI> Limtech (99.9%) in the presence of carbonaceous additive of polyethylene type.

Figure 9: Microscopy MEB of the dense ferric phosphate particles dihydrate of Budenheim E53-82 rank.

Figure 10: Triphylite synsesized starting from ferric phosphate dense particles of Budenheim rank < RTI ID=7.1> E53-82< /RTI> in the presence of carbonaceous additive of polyethylene type.

Figure 11 : 5 " cycle obtained by < RTI ID=7.2> voltamétrie< /RTI> slow < RTI ID=7.3> (80 C, < /RTI> mV. h-1) for the sample prepared starting from iron phosphate of 1 ' example 4 and starting from iron phosphate of 1 ' example 5.

Figure 12: Evolution of the capacity obtained in discharge during cycling for the sample prepared starting from iron phosphate of example 4 and starting from phosphate of 1 ' example 5 < RTI ID=7.4> (Voltamétrie< /RTI> cyclic slow
20 mV.h-1, 80 C).

Figure 13: Profiles of load and discharge obtained Pr slow voltametry (20 mV. h-1, < RTI ID=7.5> 80 D) < /RTI> of a sample of LiFePO4 produced on a pilot scale starting from FePO42H2O 6 m (reduction by CO/CO2 1/1) according to
1 ' example 7.

Figure 14: Profiles of load and discharge obtained by slow voltametry, (20 < RTI ID=7.6> mV.< /RTI> h-1, < RTI ID=7.7> 80 C)< /RTI> < RTI ID=7.8> of un< /RTI> sample of LiFePO4 prepared starting from < RTI ID=7.9> FePO42H2O< /RTI> according to 1 ' example 8.

Figure 15: Profiles of load and discharge obtained by < RTI ID=7.10> voltamétrie< /RTI> slow (20 mV. h-1, < RTI ID=7.11> 80 C)< /RTI> d'un échantillon de LiFeP04 préparé à partir de de <RTI ID=7.12> FeP042H20</RTI> according to example 9.

DESCRIPTION OF THE INVENTION

A first object of this invention is consisted a process of synthesis of composed of formula < RTI ID=8.1> C-LixMl-yM' y (X04) N, where C-représente< /RTI> carbon bridged with composed of formula < RTI ID=8.2> LiXMl-yM' y (X04) n< /RTI> in which X, y and N are numbers such as 0 < RTI ID=8.3> < X < 2, 0 Cy < 0, < /RTI> 6, and 1 < RTI ID=8.4> Cn< /RTI> < RTI ID=8.5> < 1, 5, M< /RTI> is a metal of transition or a mixture of metals of transition from the first line of the periodic table, is to Me an element of fixed valence selected among < RTI ID=8.6> Mg2+, < /RTI> Ca2+, < RTI ID=8.7> A13+, Zn2+< /RTI> or a combination of these same elements and X is selected among S, P and Si, by setting in balance in the necessary proportions of a mixture (preferentially intimates and/or homogeneous) including/understanding at least: -) a source of M has, - B) a source of an element Me; - C) a compound source of lithium; and - D) possibly a compound source of X, - E) of a source of carbon called conducting carbon sources of the elements M, Me, Li and X which can or not be introduced, in all or partly, in at least a stage, in the form of compounds comprising more than one element source, and the synthesis being done by reaction and setting in balance, thermodynamics or kinetics, of the mixture in the necessary proportions of made up the sources (also called precursors) has) with D), with a gas atmosphere, so as to preferentially impose the state of oxidation of the metal of transition to the desired degree of valence (, this valence is equal to two for iron, manganese, cobalt, nickel and three or four for titanium, vanadium) for the constitution of < RTI ID=9.1> LiXMI-yM' y (X04) N, < /RTI> by the control of the composition of the aforesaid gas atmosphere, temperature of the stage of the reaction of synthesis and rate of made up the source c) relative to the others made up sources has), b) and D); the process comprising at least a stage of pyrolysis of made up the source E) so as to obtain a compound of which the electronic conductivity, measured on a compacted powder sample, with a pressure of 3750 kg. < RTI ID=9.2> cm~2, < /RTI> is higher than < RTI ID=9.3> 10-8 S. enfl.< /RTI>

The measurement of conductivity is taken on powders of the sample. This powder (of 100 Mg with < RTI ID=9.4> lg approximately) < /RTI> is put in a hollow cylindrical mould 1,3 cm in diameter, carried out in poly (oxymethylene) < RTI ID=9.5> (Delrint))< /RTI> and it is

compacted between two stainless steel pistons using a press of laboratory to a force of 5.103 kg what corresponds to a pressure of 3750 kg. < RTI ID=9.6> cm~2.< /RTI>

The measurement of conductivity is taken by using the pistons (plungers) like electrodes and by the method of the known complex impedance of the person of the technique considered. Conductivity is obtained starting from resistance by the formula < RTI ID=9.7> ? =/i où< /RTI> R is measured resistance, and S surface (1,33 cm2 for 1,3 cm of < RTI ID=9.8> diameter), Z 1 ' epaisseur< /RTI> sample and the resistivity is determined by the formula p < RTI ID=9.9> = Rg.< /RTI>

According to an advantageous alternative, at least part of or desits metals of transition which make M finds in a state of oxidation higher or lower than that of metal in the final compound. < RTI ID=9.10> LiXMI-yM' y (XO4) n.< /RTI>

The reaction of synthesis between the compounds sources has) with D) is advantageously carried out simultaneously with the reaction of pyrolysis of made up the source E).

According to a preferential mode of realization of the synthesis according to the present invention, the reaction of pyrolysis is carried out in one second stage, consecutive with the reaction of synthesis between the compounds sources has) with D) and preferably under reducing or neutral gas atmosphere.

Compounds of formula < RTI ID=10.1> C-LiXMI~yM' y (X04) ?synthetises< /RTI> are advantageously obtained under fonne of particles and in what size and/or the shape of the particles of made up the < RTI ID=10.2> C-LixMI-yM' y (X04) n< /RTI> is < RTI ID=10.3> déterminée< /RTI> primarily by the size and the shape of the homogeneous mixture < RTI ID=10.4> et/ou< /RTI> homogeneous of the precursors used for the reaction of the synthesis and more particularly by the size and/or the shape of the precursors M and Me of departure. In this case, size of the particles of made up < RTI ID=10.5> C-LixM, - yM' y (X04) n< /RTI> obtained lies between 0,1 and 10 micrometers.

In a preferential way, size and the shape of the particles of made up < RTI ID=10.6> C-LixMI-yM' y (X04, differe< /RTI> not of more than 80% of that of the size of the precursors has) with D), preferably in which size and the form of the particles of made up < RTI ID=10.7> C-LixMI-yM' y (XO4) n< /RTI> do not differ of more than 80% of that of the precursor has) and if necessary that of the precursor b).

Selon un mode de réalisation avantageux de la présente synthèse, la teneur du composé source de carbone (appelé carbone conducteur) est choisi de façon à enrober de carbone, au moins une partie de la surface des particules du composé de formule < RTI ID= 10.8> LixM1-yM'y(XO4)n.# </RTI>

The percentage of carbon He lower than 5%, lower than 3% of the mass of is preferentially composed of formula LixM1-yM' y (XO4) N.

In a preferential way, at least 30% of the surface of the particles of composed of formula LixM1-yM' y (XO4) N are covered with carbon.

According to another advantageous mode of realization of the invention, the content of made up source of conducting carbon in the reactional medium is selected in order to bind the particles of made up the < RTI ID=11.1> LiXMI yM' y (X04) N entre< /RTI> they and to constitute agglomerates of sizes ranging between 1 and 20 microns. The percentage of dependent carbon lower than 7%, preferably lower than 5% of the mass of is then composed of formula < RTI ID=11.2> LixMI-yM' y (X04) n.< /RTI>

The process according to the invention makes it possible to control the final form of made up the < RTI ID=11.3> C-LixMI-yM' y (X04) N en< /RTI> choosing the form given to the mixture of the precursors has) with D) before synthesis. Thus, a technique used to give a form particular to the mixture of the precursors is advantageously selected in the group of the techniques of atomization, precipitation, < RTI ID=11.4> coprecipitation, < /RTI> of agglomeration and/or pelletization.

When the technique used to give a form particular to the mixture of the precursors is 1 ' atomization, the final form of made up the < RTI ID=11.5> C-LixMI-yM' y (X04) < /RTI> N obtained is that of spherical agglomerates of sizes ranging between 1 and 30 microns, the known as agglomerates consisting of smaller particles of composed of formula < RTI ID=11.6> C-LixMI yM' y (X04) n.< /RTI>

According to a preferential mode, the organic substance source of conducting carbon is selected in the group consisted polymers and oligomers containing a carbonaceous skeleton, the simple or polymeric carbohydrates and aromatic hydrocarbons.

< RTI ID=11.7> According to another < /RTI> preferential mode, the source of conducting carbon contains, in the same compound or the mixture which constitutes this source, of oxygen and the hydrogen bound chemically and whose pyrolysis releases locally from the carbon monoxide < RTI ID=11.8> et/ou< /RTI> carbon dioxide and/or hydrogen and contributing steam, in addition to the carbon deposit, to

locally create the reducing atmosphere necessary for the synthesis of the material < RTI ID=11.9> LiXMl-yM' y (X04) < /RTl> N.

In a preferential way, the compound source of conducting carbon is mainly made up of a copolymer block including/understanding at least a segment pyrolisable source of carbon and a soluble segment in < RTI ID=12.1> 1 ' eau< /RTl> and organic solvents in order to allow its distribution, preferably in a homogeneous way, around made up the < RTI ID=12.2> LiXMl-yM' y (X04) nou< /RTl> of its precursors.

Advantageously, the organic substance source of conducting carbon at least one of is made of the group consisted polyethylene, polypropylene, glucose, the fructose, the sucrose, xylose, sorbose, the starch, cellulose and its esters, the polymers blocks of ethylene ethylene and oxide and the polymers of the alcohol < RTI ID=12.3> furfurylique.< /RTl>

According to an advantageous mode of realization of the synthesis according to the present invention, the compounds sources has) with D) are in the form of powder or at least partially compacted in the form of pastilles (realized preferably continuously), in order to increase the points of contacts between the reagents and in order to increase the density of the end product while pennettant the reaction with the gas phase.

The gas phase being able to circulate in the engine in the same direction or preferentially with counter-current of the precursor supply.

Preferably, the compound source of conducting carbon is present at the time of the stage of compaction of made up has) with D).

The process of synthesis is preferentially carried out uninterrupted preferably in an engine supporting the balance of the solid powders agglomerated or not with the gas phase, for example among such engines, the revolving kilns, the fluidized beds, the furnaces with belts, the known as furnaces allowing the control of the composition and the circulation of the gas atmosphere. Dans ce cas, le débit solide est supérieur à 1 < RTI ID=12.4> kg/h,< /RTl> the temperatures preferably lie between 650 and 800 degrees
Centigrade, the time of residence is preferentially lower than 5 hours and more preferentially still lower than < RTI ID=13.1> 1/2 heure.< /RTl>

The reduction is preferentially obtained by the action of a selected reducing atmosphere in order to be able to reduce the state of oxidation of < RTI ID=13.2> the ion< /RTl> metal M at the level necessary for the constitution of composed without however reducing it at the neutral metal state.

The reducing atmosphere contains hydrogen advantageously or a gas able to generate hydrogen under the conditions of the synthesis, ammonia or a substance able to generate ammonia under the conditions of the synthesis or monoxide of carbon, these gases being used pure or in mixtures and also being able to be used in the presence of steam and/or carbon dioxide and/or in < presence; RTI ID=13.3> of un< /RTI> neutral gas (such as nitrogen or < RTI ID=13.4> 1 ' argon). < /RTI>

According to another preferential mode of realization, the reducing atmosphere is consisted a < mixture; RTI ID=13.5> CO/CO2< /RTI> or < RTI ID=13.6> H2/H20, < /RTI> < RTI ID=13.7> NH3/H20< /RTI> or their mixture, generating pressure of a lower oxygen balance or equalizes with that given by the metal of transition to the oxidation step corresponding to the precursors introduced to form the compound < RTI ID=13.8> LixMi-yM' y (X04) N, < /RTI> but higher than that corresponding to the reduction of any of the transition metals present at the metal state, ensuring the thermodynamic stability of < RTI ID=13.9> LiXMI-yM' y (X04) n< /RTI> in the reactional mixture, independently of the reaction time of the synthesis.

Preferably, the gas atmosphere is made up < RTI ID=13.10> by a mixture CO/CO2 ou< /RTI> < RTI ID=13.11> H2/H20, < /RTI> < RTI ID=13.12> NH3/H20< /RTI> or their mixture, generating a pressure of oxygen balance higher or equal to that determined by at least of the transition metals when the precursor is introduced in metal form to form the compound < RTI ID=13.13> LixMI-yM' y (X04) N, < /RTI> but higher than that corresponding to a peroxydization of the transition metals beyond their valence assigned in < RTI ID=13.14> LixMI-yM' y (X04) n< /RTI> ensuring the thermodynamic stability of < RTI ID=14.1> LiXMI-yM' y (X04) n< /RTI> in the reactional mixture, independently of the reaction time of the synthesis

The reducing atmosphere is preferentially consisted a < mixture; RTI ID=14.2> CO/CO2, < /RTI> < RTI ID=14.3> H2/H20, < /RTI> <RTI ID=14.4>NH3/H2O</RTI> or their mixture, generating pressure of a lower oxygen balance or equalizes with that given by one of metals of transition present in < RTI ID=14.5> LiXMI yM' y (X04) N, < /RTI> possibly being able to lead to the reduction of at least this transition metal at the metal state, obtaining made up the < RTI ID=14.6> LixMI-yM' y (X04) N, < /RTI> being realized by the control of the temperature and the time of contact with the gas phase or of the proportion of the precursor c) in the reactional mixture; the temperature of synthesis preferentially lying between 200 and 1.200 C, more preferentially still between 500 and < RTI ID=14.7> 800 C, < /RTI> and the time of contact of the reactional mixture with the gas

phase preferentially lying between 2 minutes and 5 hours and more preferentially still between 10 and 60 minutes.

The reducing gas atmosphere can advantageously be obtained is obtained by vacuum decomposition or under inert atmosphere, from an organic compound or a mixture of organic compound containing, bound chemically, at least of hydrogen and the oxygen, and whose pyrolysis generates monoxide and carbon and/ or a mixture of carbon dioxide and monoxide, hydrogen and/or a mixture hydrogen and vapor < RTI ID=14.8> of eau< /RTI> suitable for carry out the reduction bringing to the formation of made up the < RTI ID=14.9> LixMl-yM' y (X04) < /RTI> N.

According to a preferential alternative, the reducing gas atmosphere is obtained by partial oxidation by oxygen or < RTI ID=14.10> air, < /RTI> < RTI ID=14.11> of un< /RTI> hydrocarbon and/or of carbon, possibly in the presence of steam (preferentially steam and a content included/understood, terminals lain, between 0,1 and 10 molecules of H20 by carbon atom of 1 ' hydrocarbon), at a high temperature (preferentially ranging between 400 and 1.200 C) allowing hydrogen or the carbon monoxide formation or < RTI ID=14.12> of un< /RTI> mix carbon monoxide and hydrogen.

The gas phase consists of a gas reformed < RTI ID=15.1> in-situ< /RTI> or ex-situ. In this case, atmosphere of the gas < RTI ID=15.2> réformé< /RTI> is obtained starting from methane, propane, starting from a natural gas, or a mixture of the latter, added with air, and possibly with steam, with a predetermined partial pressure, by condensation or injection in the reformed mixture.

The heat treatment (which includes the reaction of formation of < RTI ID=15.3> LixMi-yM' y (X04) n< /RTI> and the reduction and the pyrolysis and possibly the dehydration of one or several sources have) with D)) is realized by heating from the ordinary temperature to a temperature ranging between 500 and 1.100 C. The maximum temperature reached preferentially lies between 500 and < RTI ID=15.4> 800 C.< /RTI>

According to an advantageous mode of realization of the synthesis, the time of residence of the reagents in the stage of heat treatment is lower than 5 hours, preferably lower than 1 hour.

The synthesis according to the present invention makes it possible to prepare the compound of formula < RTI ID=15.5> LiXMI-yM' y (X04) N, < /RTI> in which < RTI ID=15.6> n=l, < /RTI> of an electrochemical capacity, higher than 150 < RTI ID=15.7> mAh/g~l, mesurée< /RTI> for specific intensities higher than 10 my. < RTI ID=15.8>g-1.< /RTI>

According to an advantageous mode, the source of M causes also X and/or the source of Me causes also X and/or the source of lithium causes also
X and/or the source of X causes also lithium.

The setting in balance of the mixture of precursors has) to D) is facilitated in the form of homogeneous mixture and/or homogeneous of the solid phase and the gas phase.

Preferably, metals of transition is (are) selected (S) at least partly in the group consisted iron, manganese, cobalt and nickel, the complement of metals of transition being preferentially selected in the group consisted vanadium, titanium, chromium and copper.

Advantageously, the compound source of M is in a state of oxidation which can vary from 3 to 7.

In a preferential way, the compound source of M is the iron oxide < RTI ID=16.1> in ou< /RTI> magnetite, the dioxide of manganese, di-vanadium pentoxide, trivalent iron phosphate, < RTI ID=16.2> the hydroxyphosphate< /RTI> of iron and lithium or nitrate of trivalent iron, or a mixture of the latter.

In an advantageous way, the compound source of lithium is selected in the group consisted oxide or the hydroxide of lithium, lithium the carbonate, the neutral phosphate < RTI ID=16.3> Li3PO4, < /RTI> acid phosphate < RTI ID=16.4> LiH2P04, < /RTI> < RTI ID=16.5> the ortho, < /RTI> the méta or the poly silicates of lithium, lithium sulphate, lithium oxalate and the acetate of lithium, or a mixture of the latter. The compound source of lithium is the lithium carbonate of Li2CO3 formula.

The source of X is selected in the group consisted the sulphuric acid, lithium sulphate, the phosphoric acid and its esters, the neutral phosphate < RTI ID=16.6> Li3PO4< /RTI> or acid phosphate < RTI ID=16.7> LiH2PO4, < /RTI> phosphates mono-or < RTI ID=16.8> diammonium, < /RTI> trivalent iron phosphate, ammonium and manganese phosphate (NH4MnPO4), silica, silicates of lithium, < RTI ID=16.9> alcoxysilanes< /RTI> and their products of hydrolysis partial and mixtures of the latter. The precursory compound of X is preferentially the iron phosphate, anhydrous or hydrated.

The process according to the invention allows in particular the advantageous synthesis of one or several of derived from the lithium of formula < RTI ID=16.10> LiFePO4, < /RTI> < RTI ID=16.11> LiFe1-sMnsP04 avec< /RTI> 0 < RTI ID=16.12> #s #0, < /RTI> 9, LiFe1-7MgyPO4 and LiFe1-yCayPO4 with 0 < RTI ID=16.13> < y < 0, < /RTI> 3, < RTI ID=16.14> LiFe1-s-yMnsMgyP04</RTI> with 0 < RTI

ID=16.15> < S < 1< /RTI> and 0 < RTI ID=16.16> #y #0,2, Li1+xFeP1-xSixO4< /RTI> with 0 < RTI ID=16.17> #x #0, < /RTI> 9, < RTI ID=16.18> Lii+xFei-sMnsPi-< /RTI> < RTI ID=16.19> xSixO with 0 #s #1, Li1+zFe1-s-zMnsP1-zSzO4 with 0 #s#1, 0#z #0,2, Li1+2qFe1-s-< /RTI> < RTI ID=16.20> qMnsPO4 with 0 #s #1, < /RTI> and < RTI ID=16.21> 0 #q #0, < /RTI> 3, < RTI ID=16.22> Li1+rFe1-sMNs (S1-rPrO4) 1,5 with 0 #r #1, 0 #< /RTI> S, T < RTI ID=16.23> #1 and Li0,5+uFe1-tTit (PO4) 1,5.< /RTI> with 0 < RTI ID=16.24> #t #1 and with 0 #u #1, < /RTI> 5.

Advantageously the synthesis is applied to composed of formula < RTI ID=17.1> LiXMI-yM' y (X04) n< /RTI> who have a structure olivine or Nasicon, including the monoclinical form.

The reactional parameters are advantageously selected, in particular the kinetics of the reduction by the gas phase, so that conducting carbon is not consumed during the process of reduction.

The content of substance source of carbon conducting, present in the reactional medium subjected to reduction, is selected so that the percentage of conducting carbon in the reactional medium preferentially lies between 0,1 and 25%, more preferentially still so that it lies between 0,3 and 1,5% of the total mass of the reactional mixture.

The temperature and the duration of the synthesis are as for them selected according to the nature of the metal of transition, i.e. above a temperature minimum to which the reactive atmosphere is able to reduce the metals transition in their state from necessary oxidation in the compound < RTI ID=17.2> LixMI yM' y (X04) < /RTI> and in lower part of a temperature or a time bringing a reduction metals transition at the metal state or an oxidation from carbon resulting from the pyrolysis of the organic substance.

The heat treatment is preferentially carried out by heating from the ordinary temperature to a temperature ranging between 500 and 1.100 C, in the presence of a reducing atmosphere. In a more advantageous way, the maximum temperature reached lies between 500 and < RTI ID=17.3> 800 C.< /RTI>

Selon un autre mode avantageux, le composé <RTI ID=17.4>LixMi-yM'y (X04) n</RTI> is the < RTI ID=17.5> LIMP04< /RTI> and in which the conducting carbon rate after pyrolysis is included/understood between 0,1 and 10% in mass compared to the mass of made up the < RTI ID=17.6> LiMP04.< /RTI>

The compound source of carbon is preferentially selected in order to be easily dispersible at the time it treatment used to ensure a

homogeneous mixture with the precursors has) with D) by agitation and/or solubilization, mechanical crushing and/or ultrasonic homogenisation, in presence or not of a liquid, or by spay-drying < RTI ID=18.1> of une< /RTI> solution < RTI ID=18.2> of un< /RTI> or several precursors and or < RTI ID=18.3> of une< /RTI> suspension and or < RTI ID=18.4> of une< /RTI> emulsion.

The synthesis is particularly powerful for the preparation of the compound obtained with the fonnule < RTI ID=18.5> LiFePO4.< /RTI>

The core of the particles obtained primarily (preferably for at least 95%) consists of a compound of formula < RTI ID=18.6> LiFePO4, < /RTI> the complement advantageously primarily consisting of made up having a structure close to LiFePO4 and, in which the material obtained has a percentage of conducting carbon preferentially ranging between 0,2 and 5% compared to the mass of particles obtained.

A second object of the invention is consisted a material made up of particles comprising a core < RTI ID=18.7> et/ou< /RTI> a coating and/or a bridging, say it core including/understanding at least a compound of formula < RTI ID=18.8> C-LixMi-yM' y (X04) N, < /RTI> in which
C represents carbon bridged with made up the < RTI ID=18.9> LixMi-yM' y (X04) N, < /RTI> X, y and N are numbers such as < RTI ID=18.10> 0 vx < 2, 0 < y < 0, < /RTI> 6, and < RTI ID=18.11> 1 < n#1, < /RTI> 5, M is a metal of transition or a mixture of metals of transition from the first line of the periodic table, is to Me an element of fixed valence selected among < RTI ID=18.12> Mg2+, < /RTI> < RTI ID=18.13> Ca2+, < /RTI> < RTI ID=18.14> Al'+, < /RTI> < RTI ID=18.15> Zn2+< /RTI> et X est choisi parmi S, P et Si, ledit matériaux ayant une conductivité, supérieure à < RTI ID=18.16> 10-8</RTI> SCM-1, on a powder sample compacted with more than 3000 kg. < RTI ID=18.17> cm~2, < /RTI> preferably to 3750 kg. cm2 and whose granulometry preferably lies between 0,05 and 15 micrometers, preferably between 0,1 to 10 micrometers.

In these values of granulometry, the agglomerates of finer, possibly dependent particles are included between them by friction or decked between them by conducting carbon and forming entities, preferably quasi-spherical.

According to another mode of realization this object is consisted a material likely to be obtained by a process according to the synthesis according to the first object of the invention, comprising a core and a coating and/or a bridging, the aforementioned material presenting: - a conductivity, measured on a sample of powder compacted to 3750 kg. < RTI ID=19.1> cm~2 qui< /RTI> < is higher; RTI ID=19.2> with

10-8< /RTI> S. < RTI ID=19.3> crn 1; < /RTI> - a percentage of conducting carbon lies between 0.2 and 5%; preferably between 0.3 and 2%; and - a granulometry preferably lies between 0,05 and 15 micrometers, preferably from 0,1 to 10 micrometers.

In these values of granulometry, the agglomerates of finer, possibly dependent particles are included between them by sintering or decked between them by conducting carbon and forming entities, quasi-spherical preferences.

A third object of this request is consisted an electrochemical cell including/understanding at least two electrodes and at least an electrolyte, characterized in that at least one of its electrodes includes/understands at least one of materials according to the second object of this invention.

According to an advantageous mode, the electrolyte is a polymer, solvatant or not, optionnellement plasticized or gelled by a polar liquid containing in solution one or more metal salts.

The electrolyte is a polar liquid immobilized in a separator < RTI ID=20.1> microporeux< /RTI> and containing in solution one or more metal salts. Preferably, at least one of metal salts is a lithium salt.

According to another advantageous mode, at least one of the negative electrodes is metal lithium, a lithium alloy, in particular with aluminium, antimony, zinc, tin, possibly nanomoléculaire with lithium oxide mixes some, or a compound of insertion of carbon, in particular of graphite, a double nitride of lithium and iron, of cobalt or manganese, a lithium titanate of formula < RTI ID=20.2> $LixTi (5+3y) /4O4$, with $1 \# X \# (11-3y) /4$ (or) < /RTI> with < RTI ID=20.3> 0s y 51.< /RTI>

Advantageously, one of the positive electrodes contains one of the products likely to be obtained by a process according to the invention, used only or mixes some with a double cobalt oxide and lithium, or one with a complex oxide of formula < RTI ID=20.4> $LixNi1-y-z-q-rCoyMgzAlrO2$ with $0,1 \# X \# 1$, $0 \# < /RTI> y$, < RTI ID=20.5> z< /RTI> et r 50. 3, or with an oxide complexes of formula < RTI ID=20.6> $LixMni-y-z-q-rCoyMgzAlrO2-qFq< /RTI>$ with < RTI ID=20.7> 0.< /RTI> < RTI ID=20.8> OSSx5letOsy, < /RTI> Z, R, < RTI ID=20.9> q50.< /RTI> 3.

The polymer used to bind the electrodes or as electrolytes is advantageously a < RTI ID=20.10> polyether, < /RTI> a polyester, a polymer based on the units methacrylate of methyl, a polymer containing acrylonitrile, and/or a fluoride of < RTI ID=20.11> vinylidene, < /RTI> or a mixture of the latter.

The cell can comprise a solvent not < RTI ID=20.12> protogénique< /RTI> who includes/understands for example propylene or ethylene carbonate, a carbonate of an alkyl having from 1 to 4 carbon atoms, of < RTI ID=20.13> the y-butyrolactone, < /RTI> a < RTI ID=20.14> tétraalkylsufamide, < /RTI> a < RTI ID=20.15> ?-#< /RTI> < RTI ID=20.16> dialkyléther< /RTI> of mono, di-, sorting, tetra-but oligo-ethylene glycol of molecular weight lower or equal to 5000, as well as the mixture of above-named solvents.

The cell according to the present invention, functions preferentially like primary education or secondary generator, super-capacity or system of modulation of the light.

Advantageously, the cell of the invention functions like super capacity, then in what the material of the positive electrode is the second object of < RTI ID=21.1> the invetion< /RTI> and the negative electrode a carbon of specific surface higher than 1 < RTI ID=21.2> m2.< /RTI> < RTI ID=21.3> g-1, < /RTI> preferably higher than 5 m2. < RTI ID=21.4> g~I< /RTI> in the form of powder, of fibre or mésoporeux composite type carbon-carbon.

The electrochemical cell can also < RTI ID=21.5> fonctionner< /RTI> like system of modulation of the light and in this case, the optically inactive counter-electrode is a material according to the second object of the invention épandu in thin layer on a conducting transparent support, of type glass or polymer covered with a tin oxide doped < RTI ID=21.6> (Sn02: Sb< /RTI> or < RTI ID=21.7> SnO2< /RTI> : F) or of an indium oxide doped < RTI ID=21.8> (In203< /RTI> : < RTI ID=21.9> Sn). < /RTI>

Preferential modes
The invention suggested relates to a new way of synthesis simplified of made up the < RTI ID=21.10> LixMX04 à< /RTI> structure olivine obtained by reduction < RTI ID=21.11> of un< /RTI> mix in which at least part of the metal of transition M is in a state of oxidation higher than that of the final compound < RTI ID=21.12> LiMP04.< /RTI> Another surprising advantage of this invention is to be also compatible with the synthesis described in CA-A-2.270.771, which leads to optimized performances. In this case, the organic compound, source of carbon, are added to the mixture of the starting reagents containing at least part of the metal of transition in a state from oxidation higher than that from the compound lithium < RTI ID=21.13> LiMP04< /RTI> and the simplified synthesis leads directly to material covered with carbon ata low rate without this last not being oxidized by the reduction of the metal of state of higher oxidation. Simplification relates in particular to the reduction of the number of the stages and

especially of the number of the stages where the atmosphere should be controlled. One can refer for that with < RTI ID=22.1> the work " Modem< /RTI> Batteries ", of C. A.

Vincent, & B. Scrosati, Arnold publishers, London, Sydney, < RTI ID=22.2> Auckland, < /RTI> (1997).

The improvements also relate on the reproducibility of the synthesis, control of the size and the distribution of the particles, like on the reduction of the number and the cost of the starting reagents and of course of final material.

This synthesis, when combined with the teaching of CA-A-2.270.771, also makes it possible to control the percentage of carbon of final material.

We pay here, for the first time the synthesis of a compound < RTI ID=22.3> LiXMX04< /RTI> of olivine type, in fact < RTI ID=22.4> LiFeP04, < /RTI> realized by reduction by a gas phase of an iron III salt. Starting salts not being more sensitive to oxidation, the process of synthesis is some very simplified. Moreover the possible use of Fe203 like source of iron the cost of synthesis reduces considerably of LiFePO4. This material would then have the preference vis-a-vis other materials of cathode for battery to lithium, such as nickel or cobalt oxides in the case of the accumulators of the type lithium-ion, or the oxides of V205 vanadium or analogues less inoffensive for the environment.

LiFeP04 can be prepared starting from an iron III salt, stable with the air, for example
FeP04. < RTI ID=22.5> 2H20< /RTI> or < RTI ID=22.6> Fe203< /RTI> or of any other source of iron III. The source of lithium being for example Li2CO3 in the first case, or LiOH. < RTI ID=22.7> LiH2P04< /RTI> or < RTI ID=22.8> Li3PO4< /RTI> being used as joint source of lithium and phosphorus in the second case.

The < mixtures; RTI ID=22.9> stoechiométriques< /RTI> as well as the carbon precursor are treated with < RTI ID=22.10> 700 C< /RTI> during 4 hours under sweeping < RTI ID=22.11> of un< /RTI> excess of reducing atmosphere in order to reduce the state of oxidation of iron. The choice of the atmosphere and the temperature of synthesis is very important in order to be able to reduce iron III out of iron II without the gas atmosphere or carbon present not being able to reduce iron at the metal state. The latter will be preferentially, but in a nonlimitative way, made up for example of hydrogen, ammonia, a gas mixture able to provide hydrogen under the conditions of the synthesis, pure hydrogen being able to be used or diluted in a dry or hydrated inert gas, of carbon monoxide, possibly mixed with carbon

dioxide et/d' a dry or hydrated neutral gas. The maximum temperature of the heat treatment is selected so that carbon present is < RTI ID=23.1> thermodynamiquement< /RTI> stable visà-screw of iron II and preferably with respect to the gas phase. In the case of iron, the zone of temperature limits is located between 500 and < RTI ID=23.2> 800 C, < /RTI> preferably towards < RTI ID=23.3> 700 C.< /RTI> Beyond these temperatures, carbon becomes sufficiently reducing to reduce iron II out of metal iron. In the case of other metals of transition, any person of the trade will be able to use the curves of Ellingham to adapt the temperature and the nature of the gas atmosphere in order to obtain an equivalent result.

An unexpected aspect and surprising invention, which makes its advantage of it, is the relative chemical inertia of the carbon deposited on the surface of material compared to the reactions making it possible to reduce the oxidation step of the metal of transition, in particular, of iron. Du point de vue thermodynamique, le carbone formé par décomposition de la substance organique pyrolyse a un pouvoir suffisamment réducteur pour s'oxyder en CO2 ou CO et réduire, même sous atmosphère inerte, le Fer III en Fer < RTI ID=23.4> II,< /RTI> what would have returned the control of the content of the difficult carbon end product particularly at the low carbon rates used in the present invention. The inventors noticed that the reaction of reduction was in primarily due to the action of the reducing gas atmosphere, whose kinetics is faster than that due to the action of the carbon deposited on the surface, in spite of the intimate contact between the two phases solid (carbon and material < RTI ID=23.5> redox). < /RTI>

By employing a reducing atmosphere, preferentially containing hydrogen, of ammonia or carbon monoxide, the reduction of iron by solid carbon is not favoured < RTI ID=23.6> kinetically, < /RTI> and Iron III is Iron II tiny room mainly by reaction with the reducing atmosphere. The percentage of carbon in the end product thus corresponds practically to the output of decomposition of the organic substance, which makes it possible to control the aforementioned content.

An effect surprising of this invention, using a reaction balanced in the gas phase and the solid reagents is to be able to obtain the C< compound; RTI ID=24.1> liM' M " (XO) N with partir< /RTI> of iron of oxidation step, by using gas mixtures < RTI ID=24.2> CO/C02.< /RTI>

The following examples are given in order to better illustrate the present invention, but they could not be interpreted as constituent a limitation of the range of this invention.

EXAMPLES

1-Synthesis example of < RTI ID=24.3> LiFeP04< /RTI> starting from iron phosphate under reducing atmosphere.

LiFeP04 was prepared by reaction of FeP04. < RTI ID=24.4> 2H20< /RTI> and < RTI ID=24.5> Li2CO3< /RTI> in the presence of hydrogen. In a first stage, the < quantities; RTI ID=24.6> stoechiométriques< /RTI> of the two made up ones are crushed together in the isopropanol, then heated gradually (6 C per minute until < RTI ID=24.7> 700 C)< /RTI> in a continuous pipe still under reducing gas sweeping (8% of hydrogen in < RTI ID=24.8> F argon). < /RTI> This temperature is maintained for one hour. The sample is cooled in 40 minutes is with a speed of cooling of approximately < RTI ID=24.9> 15 C< /RTI> by minute.

During all the heat treatment and also including at the time of the descent in temperature, the reducing gas flow is maintained. The total duration of the heat treatment is of approximately 3 hours and half.

The structure of the sample was checked by diffraction X-ray and the lines correspond to those of the pure triphylite LiFeP04 and the electronic conduction of the LiFeP04 powder thus obtained compressed with 5 tons for 1,3 cm in diameter and too low to be able to be measured.

Example 1 ': Préparation de LiFeP04 enrobé de carbone synthétisé à partir de l'échantillon préparé à 1'exemple 1
The triphylite obtained with 1 ' example 1 is impregnated of an acetate solution (content of < RTI ID=25.1> 39, 7% in weight of acétyl. molecular weight average M, < /RTI> < RTI ID=25.2> from 50. 000) < /RTI> in acetone. The quantity of acetate added accounts for 5% of the weight of triphylite treated. The use of a carbon precursor in solution allows a perfect distribution on the particles of triphylite. After drying, the mixture is placed in the furnace described previously, under sweeping of an atmosphere of argon. The temperature is increased by < RTI ID=25.3> 6 C< /RTI> by minute until < RTI ID=25.4> 700 C.< /RTI> This last temperature is maintained one hour. The sample is then cooled gradually, always under argon sweeping. This sample contains 1% in carbon weight, which corresponds to an output of carbonization of acetate of 20%.

The material has an electronic conductivity of surface. The latter was measured on a compacted powder pastille. A force of 5 tons is applied during measurement to a sample 1,3 cm in diameter. Under these

conditions, measured electronic conductivity is 5.10-5 S. < RTI ID=25.5> CRA-1.< /RTI>

< example; RTI ID=25.6> 1 ": < /RTI> Comparison of the electrochemical behavior of materials prepared with examples 1 and < RTI ID=25.7> 1 ' en< /RTI> electrochemical cells.

Prepared materials with 1 ' example 1 and < RTI ID=25.8> 1 ' ont< /RTI> summer tested in piles buttons of the type CR 2032 out of batteries polymeric lithium with < RTI ID=25.9> 80 C.< /RTI> Cathodes were prepared by mixing together the powder of active material with carbon black < RTI ID=25.10> (Ketjenblacl@ ') < /RTI> pour assurer l'échange électronique avec le collecteur de courant et du poly (oxyde d'éthylène) de masse 400.000 utilisé comme agent liant d'une part et conducteur ionique d'autre part. The proportions in weight are 51: 7 : 42. Of < RTI ID=25.11> the acétonitrile < /RTI> is added to the mixture to dissolve the poly (ethylene oxide) in sufficient quantity to form a homogeneous suspension. This suspension obtained is then run on a stainless steel disc of 1 < RTI ID=26.1> cm2.< /RTI>

Cathode thus prepared is dried vacuum, then transferred out of glove compartment under atmosphere from helium (< lvppm H20, O2). A lithium sheet (27 < RTI ID=26.2> llm< /RTI> of thickness) rolled on a nickel substrate was used like anode.

The polymeric electrolyte was composed of poly (ethylene oxide) of mass 5.000.000 and < RTI ID=26.3> of un< /RTI> lithium salt of the < RTI ID=26.4> bistrifluorisulfoninimide< /RTI> Li < RTI ID=26.5> [(CF3SO2) < /RTI> 2N]) (hereafter < RTI ID=26.6> LiTFSI) < /RTI> in the proportions oxygenates units < RTI ID=26.7> oxyethylene/ions< /RTI> lithium of 20: 1.

The electrochemical experiments were led to < RTI ID=26.8> 80 C, < /RTI> temperature to which the ionic conductivity of the electrolyte is sufficient (2 < RTI ID=26.9> # 10-3 SCM-1). < /RTI>

Figure 1 shows the first cycle obtained by < RTI ID=26.10> voltamétrie< /RTI> slow, a well-known technique of the expert (20 mV. h-1) controlled by a cyclor of battery of the < type; RTI ID=26.11> Macpilet< /RTI> (BiologicTM, Claix, France), of the prepared samples with 1 ' example 1 and 1 '.

The noncarbonaceous compound of 1 ' example 1 presents the peaks < RTI ID=26.12> of oxydo-réduction< /RTI> characteristics of < RTI ID=26.13> LiFePO4.< /RTI> The capacity exchanged during the process of reduction accounts for 74% of the theoretical value. Les cinétiques de réaction sont lentes et la décharge s'étend jusqu'à 3

Volts. These limitations of capacities and kinetics of reactions are usually observed for noncarbonaceous samples of LiFeP04. The carbonaceous compound of 1 ' example 1 ' shows peaks < RTI ID= 26.14> of oxydo-réduction< /RTI> well defined and of the kinetics of reaction much faster than those of material resulting from the synthesis described in 1 ' example 1. The capacity reached in discharge is 87% of the theoretical value what represents an improvement of the capacity of the electrochemical generator of 17% compared to that of the noncarbonaceous sample of 1 ' example 1.

Example 2: Synthesis of carbonaceous LiFeP04 in a stage starting from iron phosphate under reducing atmosphere.

Carbonaceous LiFeP04 was prepared by reducing reaction of FeP04. < RTI ID= 27.1> 2H20< /RTI> and < RTI ID= 27.2> Li2C03< /RTI> in the presence of hydrogen. In a first stage, the < quantities; RTI ID= 27.3> stoechiométriques< /RTI> of the two made up ones as well as the source of carbon (acetate, (content of 39,7% of acetyl weight, molecular weight average MW of 50.000), in small proportion (5% in weight compared to the weight of < RTI ID= 27.4> FeP04< /RTI> < RTI ID= 27.5> 2H20, < /RTI> that is to say 4,2% compared to the weight of the FeP04 mixture. < RTI ID= 27.6> 2H20< /RTI> and < RTI ID= 27.7> Li2CO3) < /RTI> are crushed together in the isopropanol. The solvent is evaporated and mixes it subjected to the heat treatment described in examples 1 and 1 '. During all the heat treatment and also at the time of the descent in temperature, the reducing atmosphere is imposed by a sweeping of a mixture of hydrogen 8% in < RTI ID= 27.8> the argon.< /RTI>

The structure of the sample was checked by diffraction X-ray and the lines correspond to those of the pure triphylite LiFeP04.

The prepared sample is composed of very fine particles about the micron (figure 2). These particles are covered with a fine layer of carbon whose weight accounts for 1,2% of the total weight of the sample, measured by gravimetry after dissolution of the core of LiFeP04 in the hydrochloric acid 2M.

The material has an electronic conductivity of surface. The latter was measured according to the procedure described in example 1 '. Under these conditions, measured electronic conductivity is 2.10-3 S. cm~I.

Taking into account the residual quantity of carbon in the sample, the output of carbonization of acetate during this synthesis is 20%. It is important to note that this output is identical to that obtained in 1 ' < example; RTI ID= 27.9> 1 ' < /RTI> where the triphylite LiFeP04 is already formed and does not require any stage of reduction. It is thus obvious that carbon resulting from the decomposition of acetate is not

consumed and does not intervene in the reaction of reduction of iron III out of iron N. This reduction is thus done via the gas phase.

Example 2 ' Comparison of the electrochemical behavior of the triphylite

Carbonaceous LiFePO4 prepared with example 1 with that of a carbonaceous sample of triphylite synthesized by another way.

The prepared material with 1 ' example 2 was tested in piles buttons of the type CR 2032 described in 1 ' < example; RTI ID=28.1> 1 ". < /RTI> For comparison, we also report some results obtained for the best carbonaceous sample synthesized starting from iron II (vivianite Fe3 < RTI ID=28.2> (PO4) < /RTI> < RTI ID=28.3> 2. 8H2O) < /RTI> and whose synthesis was described before in CA-A-2.270.771.

Figure 3 presents the 5th cycle obtained by < RTI ID=28.4> voltammékie< /RTI> slow (20 mV. h-1) controlled by a cyclor of battery of the < type; RTI ID=28.5> Maepileo< /RTI> with the sample resulting from the traditional synthesis (features dotted lines) on the one hand and with that obtained example 2 (full features) of other shares. The two syntheses lead to samples having the same electrochemical behavior on the plan of the potentials of oxydoreduction and the electrochemical kinetics.

The profiles of load and discharge of batteries assembled with the sample resulting from the synthesis described in 1 ' example 2 are presented Figure 4 per two modes.

These results are obtained in galvanostatic mode between 2,8 and 3,8 Volts for two speeds of load and discharge C/8 and C/2 (the current imposed (expressed in my) at the time of the load or the discharge corresponds to 1/8 (respectively 1/2) of the theoretical capacity of the battery expressed in mAh). We reported the 20th cycle and in both cases the spill tray is flat and the capacities put in plays correspond to 95% of the theoretical capacity.

The evolution of the capacities observed in discharge during cycling during the discharge is represented Figure 5. In both cases, the initial capacity is approximately 80% of the theoretical capacity but, after ten cycles, it is higher than 95% i.e. with 160 < RTI ID=29.1> mAh. g~l, < /RTI> et reste stable sur la durée de l'expérience). These results are comparable with those obtained with the traditional synthesis (reaction of divalent iron phosphate (vivianite) with lithium phosphate).

Example 3: Control quantity of carbon

Samples of triphylite with various percentages of carbon were prepared by reaction of FePO4. < RTI ID=29.2> 2H2O< /RTI> and < RTI ID=29.3> Li2CO3< /RTI> in the presence of a < mixture; RTI

ID=29.4> CO/CO2< /RTI> 1/1 in volume. This atmosphere was selected for its reduction with respect to iron III, while maintaining a stability of iron II in particular in end of the cycle of rise in temperature of synthesis to < RTI ID=29.5> 700 C.< /RTI> In a first stage, the < quantities; RTI ID=29.6> stoechiométriques< /RTI> of the two made up ones as well as acetate are crushed together in the isopropanol. The quantities of acetate added account for 2,4 and 5% respectively weight of the mixture. After drying these mixtures are gradually heated < RTI ID=29.7> (6 C< /RTI> by minute until < RTI ID=29.8> 700 C)< /RTI> in a continuous pipe still under sweeping of reducing gas < RTI ID=29.9> (CO/CO2< /RTI> : < RTI ID=29.10> 1/1). < /RTI>

This temperature is maintained for one hour. The sample is cooled in 40 minutes is with a speed of cooling of approximately < RTI ID=29.11> 15 C< /RTI> by minute.

During all the < treatment; RTI ID=29.12> thermique< /RTI> and also including at the time of the descent in temperature, the reducing gas flow is maintained. The total duration of the heat treatment is of approximately 3 hours and half.

The structure of the samples was checked by diffraction X-ray and the lines correspond in all the cases to those of the pure triphylite LiFePO4.

Les teneurs de carbones ont été déterminées par analyse élémentaire. The results as well as electronic conductivities of the samples are deferred in table 1.
EMI29.1

% < SEP> acetate < SEP> cellulose < SEP> Content < SEP> in < SEP> C < SEP> Output < SEP> (C) < SEP> conductivity
< tb> < SEP> 0, < SEP> 62 < SEP> 0, < SEP> 22 < SEP> 2. < SEP> 10-6 < SEP> S. < SEP> cm~
< tb>
EMI30.1

< SEP> 4 < SEP> 1, < SEP> 13 < SEP> 0,2 < SEP> 1. < SEP> 10-3 < SEP> S.cm
< tb> 1, < SEP> 35 < SEP> 0, < SEP> 19 < SEP> 4 < SEP> IO-2S < SEP> cm~
< tb>
Table 1
In the three cases the output of carbonization (output (C) of table 1 of acetate is close to 20%.

The residual quantity of carbon influences in an important way electronic conductivity.

As one can note it, the quantities of conducting carbon are proportional to the quantity of added precursor (acetate). Ceci démontre d'une manière formelle que le carbone conducteur ne participe pas à la réduction du Fer < RTI ID=30.1>(III)</RTI> in the presence of reducing gas atmosphere, the latter reducing the compound of iron with faster kinetics.

Example 3 ' - Comparison of the electrochemical behavior of the samples of triphylite carbonaceous prepared to 1 ' example 3.

The prepared materials with 1 ' example 3 were tested in piles buttons of the type
CR 2032 décrites dans 1'exemple 1".

Figure 6 presents the 5th cycle obtained by < RTI ID=30.2> voltammétrie< /RTI> slow (20 < RTI ID=30.3> mV.< /RTI> h-1) controlled by a cyclor of battery of the < type; RTI ID=30.4> Macpile< /RTI> with: the sample containing carbon 0,62% (milked full) the sample containing carbon 1,13% (milked dotted lines) the sample containing carbon 1,35% (milked fatty)
The principal characteristics of the electrochemical behavior of these samples are summarized in table 2 following:
EMI31.1

% < SEP> carbon < SEP> 0, < SEP> 62 < SEP> 1, < SEP> 13 < SEP> 1, < SEP> 35
< tb> Capacity < SEP> (mAh. < SEP> g~) < SEP> 150 < SEP> 160 < SEP> 163
< tb> % < SEP> capacity < SEP> theoretical < SEP> 88 < SEP> 94 < SEP> 96.
< tb>

I < SEP> peak < SEP> (my) < SEP> 52 < SEP> 60 < SEP> 73
< tb>
Table 2
The residual quantity of carbon influences to a significant degree the capacity of the samples. Moreover, the increase in the current of peak with the carbon rate translates an improvement of the kinetics of reaction. The latter reflects the increase in electronic conductivity with the carbon rate clarified with example 3.

The way of synthesis described in example 3 makes it possible to control in a reliable and reproducible way the carbon rate in final material. What is of primary importance taking into account the influence of the carbon rate on the electrochemical properties.

Example 4 and 4 ' (Demonstration of the capacity of coating of the additive carbon of the polyethylene type and the control of the size of the particles by 1 ' coating)

Example 4 < RTI ID=31.1> LiFePO4< /RTI> is synthesized by reaction in a solid state between < RTI ID=31.2> FePO4X2H2O< /RTI> (Budenheim rank < RTI ID=31.3> E53-81) < /RTI> and < RTI ID=31.4> Li2CO3< /RTI> (Limtech 99.9%) in the presence of a carbon additive of the < type; RTI ID=31.5> polyethylene-block-poly< /RTI> (éthylène glycol) 50% oxyde d'éthylène (Aldrich) ayant une masse molaire de 1400 dissout dans < RTI ID=31.6> l'eau.< /RTI> The ferric phosphate particles dihydrate (Figure 7) have between < RTI ID=31.7> 0.< /RTI> < RTI ID=31.8> 111m< /RTI> and < RTI ID=31.9> 6pm< /RTI> of diameter. They consist of agglomerates of nano particles about < RTI ID=31.10> 50nm< /RTI> with 100nm. The ferric phosphate is mixed with lithium carbonate and is dispersed in < RTI ID=31.11> the eau.< /RTI>

The fraction of copolymer added block accounts for 3% p/p carbonate and phosphate mass used. The precursors are dispersed in a crusher with balls then dried using a spray of Niro mark. 200g of mixture is introduced into a revolving kiln in batch of < RTI ID=31.12> mark Linder balayé< /RTI> by < RTI ID=31.13> 51pm< /RTI> of a mixture of < RTI ID=32.1> CO/CO2 < /RTI> 1 : 1 molar. The gas phase < RTI ID=32.2> CO/CO2 < /RTI> 1 : 1 molar balances some with iron (II) ensures the reduction of ferric phosphate in triphylite. The temperature assembles < gradually; RTI ID=32.3> 20 C< /RTI> with < RTI ID=32.4> 700 C< /RTI> in 90 minutes then it is maintained with < RTI ID=32.5> 700 C< /RTI> during 60 minutes. The sample is then cooled of < RTI ID=32.6> 700 C< /RTI> at the ambient temperature in 30 minutes. LiFePO4 obtained starting from agglomerates of nano particles of < RTI ID=32.7> FePO4u2H2O< /RTI> dispersed in the presence of carbonaceous additive is presented at Figure 8. Le LiFePO4 conserve sensiblement la forme et la taille initiale des particules de phosphate ferrique. The carbon coating produced by the pyrolysis of the carbonaceous additive removes sintering completely and makes it possible to control the morphology of the end product. As in the preceding examples, the carbon coating improves electronic conductivity of LiFePO4 containing carbon 1% determined by ultimate analysis.

Example 5 Synthesis of dense particles

LiFePO4 is synthesized by reaction in a solid state between < RTI ID=32.8> FePO4u2H2O< /RTI> (Budenheim E53-82 rank) and < RTI ID=32.9> Li2CO3< /RTI> (Limtech 99.9%) in the presence of a carbon additive of the < type; RTI ID=32.10> polyethylene-block-

poly< /RTI> (ethylene glycol) 50% oxide of ethylene (Aldrich) having a molar mass of 1400 east dissolve in < RTI ID=32.11> the eau.< /RTI> The dense ferric phosphate particles dihydrate (Figure 9) having between 0,1pm and 201lm are mixed with carbonate of lithium and crushed in < RTI ID=32.12> the eau.< /RTI> The fraction of copolymer added block accounts for 3% p/p carbonate and phosphate mass used. The precursors are crushed in a crusher with dry balls then using a spray of Niro mark. The mixture is introduced into a revolving kiln in batch of mark

Linder swept by 5 lpm of a mixture of < RTI ID=32.13> CO/CO2< /RTI> 1 : 1 molar. The gas phase < RTI ID=32.14> CO/CO2< /RTI> 1 : 1 molar balances some with iron < RTI ID=32.15> (In< /RTI> ensure the reduction of ferric phosphate in triphylite. The temperature assembles < gradually; RTI ID=32.16> 20 C< /RTI> with < RTI ID=32.17> 700 C< /RTI> in 90 minutes then it is maintained at 700 C during 60 minutes. The sample is then cooled of < RTI ID=32.18> 700 C< /RTI> at the ambient temperature in 30 minutes. LiFePO4 obtained starting from the < RTI ID=32.19> FePO4#2H2O< /RTI> dense crushed in the presence of carbonaceous additive is presented at Figure 10. The ultimate analysis indicates that it contains 1.2% C. By comparison, the typical morphology of the < RTI ID=33.1> LiFePO4< /RTI> de la < RTI ID=33.2> FigurelO< /RTI> is denser and less porous than LiFeP04 of the Figure < RTI ID=33.3> 8< /RTI> and appreciably retains the shape and the size of the particles of the precursor < RTI ID=33.4> FeP04< /RTI> < RTI ID=33.5> 2H20), < /RTI> illustrated on Figure 9. The products of reaction of examples 4 and 5 have a granulometry connect average similar mainly made up of particles having between 0, < RTI ID=33.6> 1, um and 6pm< /RTI> of diameter which differs by their more or less porous density depending on the starting precursors.

The carbonaceous additives of polyethylene type coat the grains with ferric phosphate during drying by atomization. During the heat treatment, the carbonaceous additive pyrolysis and coats the particles with a fine layer of carbon. This layer of carbon completely removes sintering thus preserving the shape and the initial size of ferric phosphate of the mixture of precursor after crushing with lithium carbonate. The carbonaceous additive makes it possible to control the agglomeration of final LiFeP04 by removing sintering during the heat treatment. The particles formed starting from dense ferric phosphate present a higher compactness and pennet the manufacture of dense electrodes (?loading?). By dense electrode one understand here a great quantity of matter activates < RTI ID=33.7> (LiFeP04) < /RTI> by voluminal unit. As in the preceding examples, the coating of this fine layer of carbon improves electronic conductivity of the product

and increases the electrochemical performances of the composite electrode.

6-Comparison example of the electrochemical behavior of materials prepared with examples 4 and 5 in electrochemical cells.

The materials prepared with examples 4 and 5 were tested in piles buttons of the type CR 2032 out of batteries polymeric lithium with < RTI ID=33.8> 80 C.< /RTI> Cathodes were prepared by mixing together the powder of active material with carbon black < RTI ID=33.9> (Ketjenblack) < /RTI> to ensure the electronic exchange with the collector of current and the poly (ethylene oxide) of mass 400.000 used as agent binding on the one hand and ionic driver on the other hand. The proportions in weight are 51: 7 : 42. Of < RTI ID=33.10> the acétonitrile< /RTI> is added to the mixture to dissolve the poly (ethylene oxide) in sufficient quantity to form a homogeneous suspension. This suspension obtained is then cast on a stainless steel disc of L, cm2. Cathode thus prepared is dried vacuum, then transferred out of glove compartment under atmosphere from helium (< lppm H20, O2). A lithium sheet (27 m) rolled on a nickel substrate was used like anode. L'électrolyte polymère était composé de poly (oxyde d'éthylène) de masse 5.000.000 et de sel de lithium de la < RTI ID=34.1> biskifluorisulfoninimide< /RTI> Li < RTI ID=34.2> [(CF3SO2) < /RTI> 2N]) (hereafter < RTI ID=34.3> LiTFSI) < /RTI> in the proportions oxygenates units < RTI ID=34.4> oxyethylene/ions< /RTI> lithium of 20: 1.

The electrochemical experiments were led to < RTI ID=34.5> 80 C, < /RTI> temperature to which the ionic conductivity of the electrolyte is sufficient (2 X < RTI ID=34.6> 10-3 Scni I). < /RTI>

Figure 11 shows the first cycle obtained by slow voltametry, a well-known technique of the expert (20 mV. h-1) controlled by a cyclor of battery of the < type; RTI ID=34.7> Macpile# < /RTI> < RTI ID=34.8> (Biologicrm, < /RTI> Claix, France) of the samples prepared with examples 4 and 5 with a ipic of approximately 70mA/g. The two samples present excellent electrochemical performances in cycling, to see Figure 12.

Example 7: - Production continues out of electric revolving kiln
One mixes ferric phosphate dihydrate < RTI ID=34.9> (FeP04-2H20) < /RTI> of Budenheim (rank
E53-81) (Figure 7) in < quantity; RTI ID=34.10> stoechiométrique< /RTI> with lithium < carbonate; RTI ID=34.11> (Li2CO3) < /RTI> of Limtech (99.9%) using a crusher with balls in < RTI ID=34.12> the eau.< /RTI> The ferric phosphate dihydrate is presented in the form of fine powder having elementary particles between 0, < RTI ID=34.13>

1 um< /RTI> and < RTI ID=34.14> 6pm< /RTI> of diameter. These elementary particles are made of agglomerates of nano particles. Copolymer polyethylene-blockpoly (ethylene glycol) as described to 1 ' example 4 is added like carbon additive improving conductivity of the end product by pyrolysis during the heat treatment of the mixture of precursor. The copolymer block mass is equivalent to 3% p/p of the quantity of ferric phosphate and lithium carbonate. Les quantités suivantes de réactifs sont utilisées : < RTI ID=34.15> FePO4# 2H2O< /RTI> (Budenheim rank < RTI ID=34.16> E53-81) 40 kg< /RTI> < RTI ID=34.17> Li2C03< /RTI> (Limtech 99. 9%) = 7.91 kg
Copolymer PE/POE = 1.44 kg
Demineralized water 40 liters
Le mélange est séché à l'aide d'un atomiseur de marque Niro puis alimenté dans un four rotatif de marque ABB-Raymond. The revolving kiln has < RTI ID=35.1> 16.< /RTI> < RTI ID=35.2> 5cm< /RTI> of diameter by 3m length. The mixture of precursors is fed at a rate of 1.4 kg/h in order to obtain a production of approximately < RTI ID=35.3> Ikg/h< /RTI> of LiFeP04 for one 34 hours period. The flow of precursors is adjusted so that the percentage of filling of the furnace does not exceed 8% of the internal volume of the furnace thus ensuring the uniformity of mixing and the exchange with the gas phase during the heat treatment. A gas mixture balances some with iron < RTI ID=35.4> (In< /RTI> is introduced into the furnace with counter-current of the mixture of precursors. The reduction of iron < RTI ID=35.5> (m) < /RTI> out of iron < RTI ID=35.6> (11) < /RTI> is led by
CO/CO2 diluted in nitrogen in the following proportions:
3 < RTI ID=35.7> Ipm of CO< /RTI>
2.4 lpm of C02
15 N2 lpm
The revolving kiln turns to 2 rpm with an angle of < RTI ID=35.8> 1.< /RTI> The mixture enters the cold zone to < RTI ID=35.9> 200 C< /RTI> then goes up to < RTI ID=35.10> 700 C< /RTI> in 80 minutes (6.3 C/minutes). The calcined product remains with < RTI ID=35.11> 700 C< /RTI> during 40 minutes then cooled < RTI ID=35.12> 700 C< /RTI> at the ambient temperature in 40 minutes. The recovered product contains 0.9% of carbon produced by the pyrolysis of polymer containing polyethylene. An analysis X-ray confirms that the product is triphylite. Les particules élémentaires de 0,1 <RTI ID=35.13> pm à 6 pm</RTI> have an average diameter < RTI ID=35.14> (dso) < /RTI> of approximately < RTI ID=35.15> 2, um.< /RTI> They are made of agglomerates of nano particles of a few tens of nanometers similar to the starting product. The nano partially sintered particles support a < RTI ID=35.16> bonne< /RTI> density of current by their great specific

surface. Moreover carbon coating supports a high electronic conductivity, criterion essential with the manufacture of electrode presenting a density running high and an output close to the theoretical yield of the < RTI ID=35.17> LiFePO4, < /RTI> I. E.

< RTI ID=35.18> 170 mAh/g.< /RTI>

The prepared material was tested in piles buttons of the type CR 2032 described in 1 ' example 6 and shows an output of 96% (164 mAh/g) illustrated on Figure 13.

Reducing 8-Gas example starting from combustion partial of natural gas
LiFePO4 is synthesized by reaction in a solid state between the < RTI ID=36.1> FePO4#2H2O< /RTI> of
Budenheim (E53-81 rank) and < RTI ID=36.2> Li2CO3< /RTI> of Limtech (99.9%) in the presence of a carbon additive of the < type; RTI ID=36.3> polyethylene-blocIbpoly< /RTI> (ethylene glycol) 50% oxide of ethylene (Aldrich) having a molar mass of 1400 dissolve in < RTI ID=36.4> the eau.< /RTI> Ferric phosphate particles dihydrate having between 0.1 m and 6 m are mixed with carbonate of lithium and crushed in < RTI ID=36.5> the eau.< /RTI> The fraction of added copolymer accounts for 4% p/p carbonate and phosphate mass used. The precursors are dispersed in a crusher with balls then dried using a spray of mark
Niro. The mixture is introduced into a revolving kiln in batch of Linder mark. A reducing mixture of natural gas partially burned in the presence of air in an external reformor. It is then introduced into the furnace at a rate of 5 < RTI ID=36.6> lpm.< /RTI> The gas mixture is generated independent by mixing natural gas (methane) and < RTI ID=36.7> the air< /RTI> dans une proportion 1 : 5. The analysis of the gas mixture shows the following concentrations; < RTI ID=36.8> 14% H2, 14% H2O, 11% CO, 3% CO2< /RTI> and < RTI ID=36.9> 58% N2.< /RTI> The temperature assembles < gradually; RTI ID=36.10> 20 C< /RTI> with < RTI ID=36.11> 700 C< /RTI> in 90 minutes (7.6 C/minute) then it is maintained with < RTI ID=36.12> 700 C< /RTI> during 60 minutes. The sample is then cooled of < RTI ID=36.13> 700 C< /RTI> at the ambient temperature in 30 minutes. The product obtained is similar to that of Figure 8. An analysis X-ray shows the structure olivine of the triphylite. The ultimate analysis indicates that the sample contains 1.5% of carbon.

The prepared material was tested in piles buttons of the type CR 2032 described in 1 ' example 6. < RTI ID=36.14> Il< /RTI> show an output from approximately 92% (155mAh/g), to see Figure 14.

Reducing 9-Gas example starting from combustion partial of propane
The < is synthesized; RTI ID=37.1> LiFePO4< /RTI> by reaction in a solid state enters the ferric phosphate dihydrate Budenheim (E53-81 rank) and lithium (Limtech 99.9%) carbonates it.

The two precursors are mixed in < quantities; RTI ID=37.2> stoechiométriques< /RTI> then dispersed in < RTI ID=37.3> 1 ' eau< /RTI> using a crusher with balls. A carbonaceous additive of < type; RTI ID=37.4> polyethylene-< /RTI> block-poly (ethylene glycol) soluble in < RTI ID=37.5> 1 ' eau< /RTI> is added in the mixture during crushing. La fraction de copolymère ajouté représente 4% p/p de la masse de phosphate et de carbonate utilisé. This additive will carbonize during the heat treatment of the mixture and will deposit a thin layer of carbon on the surface of the particles.

For this example, the following quantities of reagents are used: < RTI ID=37.6> FePO4'2H2O< /RTI> (Budenheim E53-81) < RTI ID=37.7> = 100 kg< /RTI> < RTI ID=37.8> Li2CO3< /RTI> (Limtech 99. 9%) = 19.78 kg
Copolymer PE/POE = 4.79 kg
Demineralized water 100 liters
The dispersed mixture in a very homogeneous way using a horizontal crusher with balls containing of the steel balls of 2mm of diameter is dried by a spray (?spray-dryer?) of Niro mark. < RTI ID=37.9> 11< /RTI> is then fed in a revolving kiln with the gas propane (?direct fired rotary drill kiln?) of mark Bartlett & Snow. The furnace has 38.1cm internal diameter by < RTI ID=37.10> 4m80< /RTI> of length interior. The mixture of precursor is fed with against current of gas in the rotary kiln with 3 rpm with an angle of < RTI ID=37.11> 1. < /RTI> The atmosphere balances some with iron < RTI ID=37.12> (IT) < /RTI> is generated in situ by combustion partial of the propane fed in the burner of 500000 BTU. For each mole of gas propane injected into the furnace, 13 moles of air (equivalent to 2.75 moles of oxygens) are injected in order to burn gas partially and to generate a reducing atmosphere allowing the reduction of ferric phosphate in triphylite.

The chemical composition of the gas phase generated in situ is 13.6% CO, 3.2% < RTI ID=37.13> CO2, < /RTI> 12% < RTI ID=37.14> H2, < /RTI> 11.2% H2O and 60% N2.

The mixture is fed with < RTI ID=38.1> 5kg/h< /RTI> during 25 hours. It enters the furnace to approximately < RTI ID=38.2> 200 C< /RTI> then goes up gradually until approximately < RTI ID=38.3> 700 C< /RTI> to 5 C/minutes in order to support a complete reaction of the precursors. The product remains approximately 15 minutes with approximately < RTI ID=38.4> 700 C.< /RTI> LiFePO4 is presented in

the form of fine blasting powder not agglomerated containing 1.5% of carbon produced by the pyrolysis of the carbon additive of the polyethylene type. The fraction of carbon is obtained by ultimate analysis.

The prepared material with 1 ' example 9 was tested in piles buttons of the type CR 2032 described in 1 ' example 6. Figure 15 shows that the material with an output of 90% with a ipic of approximately 75mAh/g.

Example 10: - preparation of LiFe0.5Mn0.5PO4 under reducing atmosphere.

< RTI ID=38.5> LiFeo.< /RTI> 5Mno. < RTI ID=38.6> 5P04< /RTI> was prepared by mixing the stoechiometric quantities of < RTI ID=38.7> LiH2P04, < /RTI> < RTI ID=38.8> FeC204.</RTI> < RTI ID=38.9> 2H20< /RTI> and < RTI ID=38.10> (CH3COO) < /RTI> 2Mn. 4H20. These compounds are crushed in heptane. After drying the mixture is heated gradually until < RTI ID=38.11> 400 C< /RTI> under air to break up the groupings acetates and oxalates. This temperature is maintained for 8 hours. During this treatment, iron II iron oxide III. The mixture is then < RTI ID=38.12> rebroyé< /RTI> in an acetone solution containing the carbon precursor (acetate 39.7% in weight of groupings acétyls) 5% in weight compared to the mixture). After drying, the mixture is treated thermically under a sweeping of < RTI ID=38.13> CO/CO2< /RTI> 1/1 following the protocol describes to 1 ' example 3.

The final compound contains carbon 0.8%. Its electronic conductivity is 5.10-4 S. < RTI ID=38.14> cm~l mesuré< /RTI> according to the technique described with example 1. The electrochemical behavior of the sample < RTI ID=38.15> LiFeo. 5Mno. 5P04< /RTI> was evaluated at ambient temperature out of battery lithium containing a liquid electrolyte.

Cathodes consist of a mixture of active matter, of flexible agent and carbon black, (PVDF in solution in the < RTI ID=38.16> N-méthyl< /RTI> pyrolidone) in proportions 85: 5 : 10. The composite is extended on a collector of aluminium current. After drying, electrodes of 1,3 cm2 and a capacity of approximately 1,6 mAh are cut out with the punch. The batteries are assembled out of glove compartment, under inert atmosphere.

Measurements were carried out in an electrolyte containing LiC104 1M in a mixture EC.: DMC 1: 1. The anode consists of lithium. The tests are carried out at ambient temperature.

Figure 16 presents and the discharge load diagrams of a battery < RTI ID=39.1> cyclée< /RTI> in galvanostatic mode between 3 and 4.3 Volts. The modes of imposed load and discharge correspond to C/24 (the battery is charged of 24 hours then discharged for the same length of time)

La courbe de décharge possède deux plateaux : the first towards 4V corresponds to the reduction of Manganese III out of manganese II, and the second towards 3.4 V corresponds to the reduction of iron III out of iron < RTI ID=39.2> II.< /RTI> The specific capacity obtained during the discharge is 157 mAh. g-1, which corresponds to 92% of the theoretical capacity.

Example: 11- :
The compound < is produced; RTI ID=39.3> C-LixMl-yM' y (X04) n< /RTI> on the basis of an iron powder of size of a few microns, < RTI ID=39.4> LiH2P04< /RTI> and of the additive carbon (copolymer) conducting as used in the preceding examples.

These reagents are closely mixed by crushing of an atmosphere made up of a mixture 1: 1 de <RTI ID=39.5> CO/CO2.< /RTI>

The presence of made up LiFeP04 is confirmed by the diagram of diffraction of x-rays obtained starting from the powder thus obtained.

Example 12 Controls morphology by atomization < RTI ID=40.1> LiFeP04< /RTI> is synthesized by reaction in a solid state between < RTI ID=40.2> FeP04* 2H20< /RTI> (Budenheim rank < RTI ID=40.3> E53-81) < /RTI> and Li2CO3 (Limtech 99.9%) in the presence of a carbonaceous additive derived from cellulose. The ferric phosphate particles dihydrate have between 0. 1 m and < RTI ID=40.4> 611m of diamèke.< /RTI> The ferric phosphate is mixed with lithium carbonate and is dispersed in < RTI ID=40.5> the eau.< /RTI> A carbon additive of the type hydroxyethyl cellulose (Aldrich) is dissolved in < RTI ID=40.6> the eau.< /RTI> The fraction of added cellulose accounts for 6% p/p carbonate and phosphate mass used. The precursors are dispersed in a crusher with dry balls then using a spray laboratory of Buchi mark equipped with a tube under pressure. The mixture is introduced into a revolving kiln in batch of Linder mark swept by a mixture of CO/CO2 1: 1 molar. The gas phase < RTI ID=40.7> CO/CO2 1< /RTI> : 1 molar balances some with iron (II) ensures the reduction of ferric phosphate in triphylite. The temperature assembles < gradually; RTI ID=40.8> 20 C< /RTI> with < RTI ID=40.9> 700 C< /RTI> in 90 minutes then it is maintained with < RTI ID=40.10> 700 C< /RTI> during 60 minutes. The sample is then cooled of < RTI ID=40.11> 700 C< /RTI> at the ambient temperature in 30 minutes. The < RTI ID=40.12> LiFeP04, < /RTI> obtained starting from < RTI

ID=40.13> FePO4# 2H2O< /RTI> and of < RTI ID=40.14> Li2CO3<
/RTI> dispersed and dried by atomization in the presence of
carbonaceous additive derived from cellulose, is presented at Figure
17. It is noted that drying by atomization of the mixture of precursors
makes it possible to control the size and the morphology of the end
product. It makes it possible to produce spherical agglomerates of the
desired size. It is known that one can adjust the size of the
agglomerates by varying the parameters of atomization such as the
type of tube (under pressure " presses nozzle ", rotary " rotary drill "
or Bi-fluid " two-fluid "), the solid percentage of the mixture, the
viscosity and the temperature of injection, etc.

L'enrobage de carbone améliore la conductivité électronique de cet
échantillon de
LiFePO4 containing carbon 1,09% determined by ultimate analysis and
having a conductivity of 2.10-3S. < RTI ID=40.15> cm1< /RTI>
measured according to the technique described with the < example;
RTI ID=40.16> 1.< /RTI>
The prepared material was tested in a pile button of the type CR 2032
described in the preceding examples. It has a capacity equivalent to
92% of the theoretical capacity, I. E. 156 < RTI ID=41.1> mAh/g.<
/RTI>

Example 13. Coating and bridging of the particles of < RTI ID=42.1>
LiFePO4< /RTI> by carbon
LiFePO4 is synthesized by reaction in a solid state between < RTI
ID=42.2> FePO4) 2H20< /RTI> (Budenheim E53-81 rank) and < RTI
ID=42.3> Li2CO3< /RTI> (Limtech 99.9%) in the presence of a
mixture of carbonaceous additives. The ferric phosphate particles
dihydrate have between < RTI ID=42.4> 0.< /RTI> < RTI ID=42.5>
1pm< /RTI> and 6pm of diameter. The ferric phosphate is mixed with
lithium carbonate and is dispersed in < RTI ID=42.6> the eau.< /RTI>
Le mélange d'additif de carbone contient du < RTI
ID=42.7> polyéthylene-</RTI> block-poly (ethylene glycol) as
described in the preceding, dissolved examples in the isopropanol and
of acetate. The fraction of polyethylene-blockpoly (ethylene glycol)
added accounts for 1% p/p carbonate and phosphate mass while the
fraction of acetate accounts for 4% of the carbonate and phosphate
mass. The precursors are crushed in a crusher with dry balls then. The
mixture is introduced into a revolving kiln in batch of mark
Linder swept by a mixture of 5 lpm of < RTI ID=42.8> CO/CO2<
/RTI> 1 : < RTI ID=42.9> 1< /RTI> molar. Gas phase CO/CO2 1: <
RTI ID=42.10> 1< /RTI> molar balances some with iron (II) ensures
the reduction of ferric phosphate in triphylite. The temperature
assembles < gradually; RTI ID=42.11> 20 C< /RTI> with < RTI

ID= 42.12> 700 C< /RTI> in 90 minutes then it is maintained with < RTI ID= 42.13> 700 C< /RTI> during 60 minutes.

The sample is then cooled of < RTI ID= 42.14> 700 C< /RTI> at the ambient temperature in 30 minutes.

LiFeP04 observed by microscopy with electronic transmission is presented at figure 18. This figure shows particles not sintered but coated and decked by carbon, obviously confirming the close physical link between carbon and LiFePO4. This bridging. allows to manufacture agglomerates of

LiFeP04 bound by carbon. Coating and bridging by carbon improve electronic conductivity of composite cathodes manufactured starting from this sample of LiFeP04 containing 1.12% of carbon determined by ultimate analysis and having an excellent conductivity of 3.10-2S. < RTI ID= 42.15> Cn-L mesuré< /RTI> according to the described technique with 1 ' example 1.

The prepared material was tested in a pile button of the type CR 2032 described in the preceding examples. It has a capacity equivalent to 97% of the theoretical capacity (164 mAh/g) with an excellent density of current.